

Ligand effects on the electronic structure and magnetism of magnetite surfaces

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Abstract

We address the effect of functionalization on the electronic and magnetic properties of magnetite surface as an indicator of the same properties in nanoparticles too big for a direct ab-initio approach. Using well-established methods and references (namely LDA+U on magnetite surfaces) we could verify the validity of our approach, and using two typical ligands, dopamine and citrate, namely π and σ electron donors, we could predict that those ligands would induce a different change in the electronic properties of the systems, but in both cases an enhancement of magnetization.

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I. INTRODUCTION

During the last decade, strong efforts have been devoted to studying magnetic iron oxide nanoparticles, which present promising applications in various fields, especially in medicine, for instance as contrast agents in MRI, drug delivery vectors, or as heat mediators in hyperthermia treatments. Maghemite (γ Fe_2O_3) and magnetite (Fe_3O_4) nanoparticles, besides their low cost, high chemical stability and low toxicity, have extremely interesting properties due to the high magnetic moments caused by their ferrimagnetism. Under a certain size, those nanoparticles present zero coercivity¹ which makes them particularly useful due to the apparition of superparamagnetism and the prevention of the clogging of particles. In hyperthermia treatments, the application of an alternating field on top of a strong static magnetic field leads to heat dissipation by hysteresis losses. Once again, a rather small size of nanoparticles seems to be optimal, about 20 nm in the case of magnetite, for instance^{2,3}. Some authors⁴ have even suggested the possibility of engineering nanoparticles to exhibit a Curie temperature close to the therapeutic one so that their heating power switches off above this desired temperature.

Besides, the question of the biocompatibility of nanoparticles arise. Various means of surface manipulation of the nanoparticles are used, such as the use of ligands, layers of polymers or of other materials such as proteins⁵. The first goals are to make the particles hydrophilic, then to make them biocompatible, by reducing their sensibility to the pH of the solution in which they are used. The next issue is to target them to tumors by adding specific ligands⁶. The question then arises of the change induced on the physical properties of the nanoparticles by the presence of a specific ligand.

Among those changes, the question of the charge order at the surface of the nanoparticles is a crucial one since it can influence magnetic as well as conduction properties. A series of recent papers has successfully addressed, for instance, the theoretical and experimental descriptions of charge order and Verwey transition in bulk magnetite^{7,8} or nanocrystals⁹ as well as magnetite surface^{10,11,12}. Magnetite is at room temperature a poor metal, the electronic conductivity being caused by the t_{2g} orbitals contributed by the so-called octahedral Fe(B), randomly distributed, cations. Various models have been proposed to describe the magnetite surface¹³, but recent DFT approaches^{12,14-17} seem to be the most promising for iron oxide surfaces, as for iron oxide clusters¹⁸.

In this paper, we propose to extend those studies in order to address the role of commonly used ligands on the charge order at the surface of magnetite and their effect on the magnetic and electronic properties of this material. If the radius of the nanoparticles used in medicine is large enough, we argue that the local effects are indistinguishable from surface effects.

II. METHOD AND CHOSEN SYSTEMS

We chose to describe the systems by density functional theory, using a well-established combination of plane waves and pseudopotentials, since core electrons do not contribute to the phenomena we are interested in, and since periodicity is assumed in two directions at least to describe surfaces, a large enough vacuum being added in the third direction in order to minimize interactions in between periodic replicas.

The magnetite surface was thus built by taking the unit cell from^{19,20} adding 3.4 nm of vacuum in the [001] direction and structurally annealing it with the PWscf program from the Quantum Espresso suite²¹.

We used the LDA+U method for magnetite (in order to have an state presenting a very small gap, as reported elsewhere in the literature²²). We used Marzari-Vanderbilt smearing and a Gaussian smearing factor of 0.02. a 0.17 mixing factor for self-consistency was used. The LDA+U parameters were set at $U=4.5$ eV for Fe and $J=0$ in accordance with previous papers^{12,22}. We used an automatic sampling of the first Brillouin zone. No symmetry was used. Due to the corresponding very high computational cost, at first we used an energy cut-off of 27 Ry and turned off the spin degree of freedom in order to explore the structural stability of the system, and progressively increased this cutoff to a value of 30 Ry which we found not to perturb the results, as well as using a grid of 4X4X4 K-points in the first Brillouin zone. Correspondingly, we turned on the spin degree of freedom in the calculation after having established stable structures, and even checked that the result was the same up to two decimals in various observables when using non-collinear magnetism, showing that the systems are essentially collinear ferrimagnets.

We used standard ultrasoft pseudopotentials from the Quantum Espresso distribution using the Perdew-Wang 91 functional in LDA+U²³. Using this method, we could check that the magnetite crystal cell from^{19,20} was structurally stable, , that we could reproduce the density of states from²², and that the magnetite surface, using 3.4 nm of vacuum in the [001]

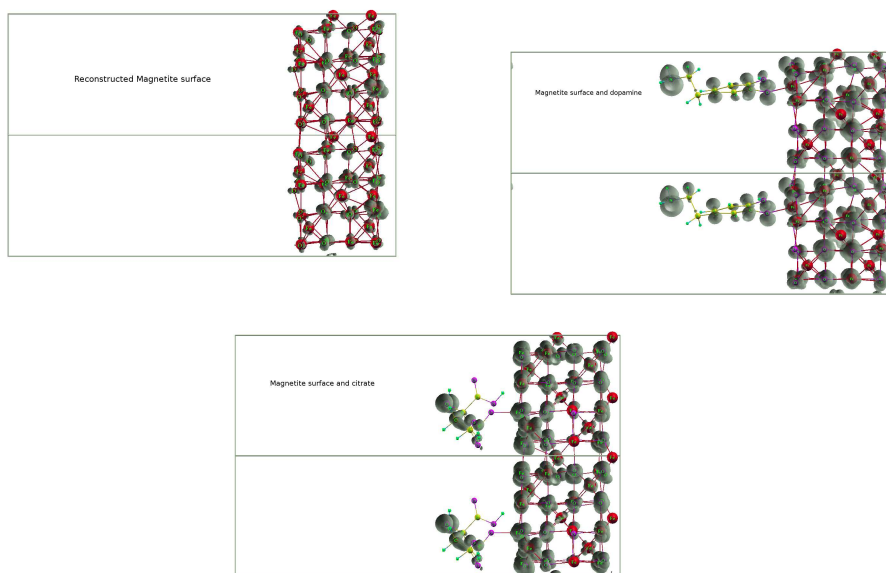


FIG. 1: Three dimensional view the surfaces studied. Bonds are drawn using the default parameters of the XCrysden program, and an electronic isosurface at the Fermi energy is drawn at 7% of the maximum value in each case.

direction, was subject to small structural changes but that the corresponding total density of states was similar to the one of¹². The magnetite surface is represented on figure 1 and the corresponding total density of states on figure 2.

We first modeled the ligands we chose to study using the WebMO interface to the Gaussian09 code²⁴ using the Hartree-Fock method with the Hartree-Fock method with 6-31+G(d) basis set which is often considered as the best compromise between speed and accuracy in order to perform a quick structural optimization of such molecules. We then checked that the obtained coordinates for the ligands corresponded to stable molecules in the pseudopotential approach, added one of those molecules at 1.5 nm of the magnetite surface optimized as described above, and performed a full structural optimization going to 0 K by the standard annealing method of the PWScf code.

We chose two type of commonly used ligands : first, a π -electron donor type for which we chose dopamine as commonly used in experimental work trying to make nanoparticles biocompatible as described in the introduction, then a σ -electron donor for which we chose citric acid, a molecule also widely experimentally used^{2,25}. A better description would of

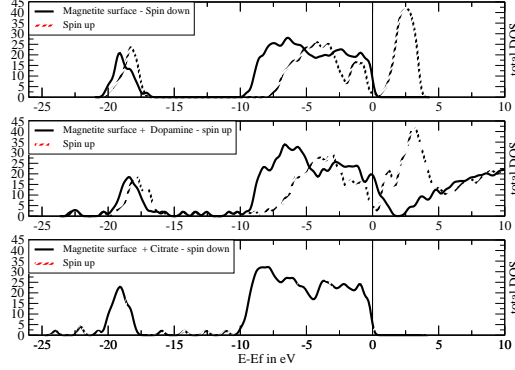


FIG. 2: Total density of states for the three chosen systems

course include water molecules or even charges in order to model pH effects, but with about 500 active electrons and 100 atoms, as well as 250000 G-vectors and no symmetry we feel that the system is at the limit of what is nowadays computationally tractable.

III. RESULTS AND DISCUSSION

We present on figure 1 a view of three typical results for the atomic positions. On these results, it is clear that dopamine has a preferential adsorption site at the octahedral (A) iron atom of the magnetite surface, when the citrate ligand has a preferential binding on the tetrahedral (B) site of the magnetite surface.

This can be attributed to the presence of an aromatic cycle in dopamine and π electrons close to the hydroxyl group. From the total density of states plotted on figure 2, one can see that the presence of dopamine does change the small gap of magnetite by adding some conduction electrons, when the presence of citrate does not significantly changes the total density of states. The difference of spin up and down density of states led us to suspect an effect of functionalization on magnetization of the systems.

Those results are summarized on table I. Functionalization leads to a marked increase in magnetism, when the value of magnetite surface alone is close to the one obtained by¹². This increase in magnetic momenta can be compared to results recently experimentally obtained by²⁶.

Besides, in order to elucidate the role of d orbitals on iron atoms on those effects, we plot on figure 1 typical electronic densities isosurfaces at Fermi energy. One can see on those figures the typical π character of orbitals contributed by dopamine to conduction electrons

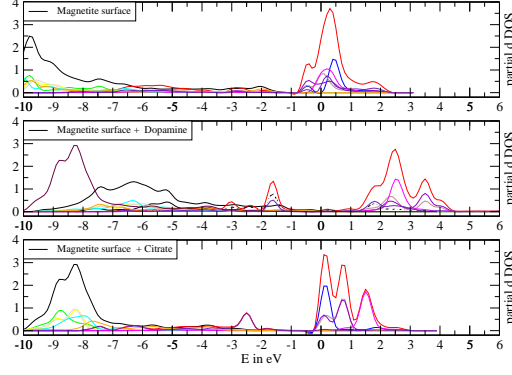


FIG. 3: Partial density of states projected on a "d" state for an atom of type (A) at the magnetite surface, where dopamine preferentially binds

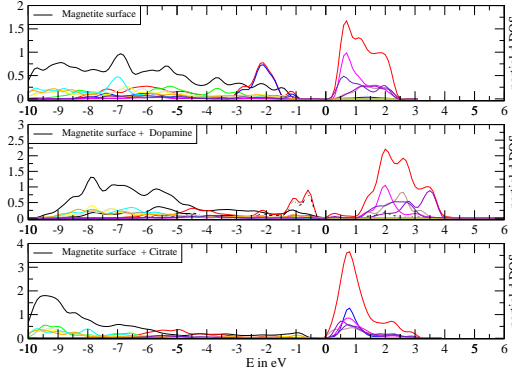


FIG. 4: Partial density of states projected on a "d" state for an atom of type (B) at surface, where citrate preferentially binds

at the surface, versus the lack of contribution of the citrate ligand. In both cases, there is however a change of the d character of the electrons contributing to conductivity close to the surface, when in the case of the non-functionalized magnetite surface the conductivity rather comes from bulk electrons. Those results remind us of those obtained by¹⁷ about the change in the conducting behavior of magnetite induced by hydrogen adsorption, turning from a semiconductor to a half-metal.

In order to further analyze those results, we plot on figure 3 and 3 projected densities of states for two typical atoms, namely Fe atoms of octahedral (A) types and tetrahedral (B) types where, respectively, dopamine and citrate prefer to bind at the magnetite surface. Only d -character wavefunctions are plotted around the chosen atoms, and one does see that the presence of either dopamine or citrate leads to a marked change in the projected densities of states around the chosen atoms, the presence of dopamine shifting the positions

System	Magnetite s.	W.Citrate	W.Dopamine
Fermi energy	-1.2550 eV	-0.4523 eV	-0.6216 eV
Total mag.	75.03 μ_B /cell	92.69 μ_B /cell	83.46 μ_B /cell
Absolute mag.	83.67 μ_B /cell	97.17 μ_B /cell	90.90 μ_B /cell

TABLE I: Some quantitative results obtained on the chosen systems

of the peaks when the presence of citrate mainly changes the shapes of the peaks. From this we conclude that the functionalization by dopamine will induce a stronger change in the magnetic properties of the system than the one by citrate, which, however, tends to induce a stronger magnetization.

IV. CONCLUSION

In this paper, we address the effect of functionalization on the electronic and magnetic properties of magnetite surface as an indicator of the same properties in nanoparticles too big for a direct ab-initio approach. Using well-established methods and references (namely LDA+U on magnetite surfaces) we could verify that we had similar results to those in recent papers on magnetite surfaces, and using two typical ligands, π and σ electron donors, we could predict that those ligands would induce a different change in the electronic properties of the systems, but in both cases an enhancement of magnetization. These findings are confirmed by some recent experimental work. The present study could however be improved by looking at temperature and solvent effects, by using a larger number of atoms in order to be closer to experimental systems, as well as by modeling some other changes in physical properties of magnetic nanoparticles of medical interest induced by surface functionalization.

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